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Preparation of $Ba_2Ti_9O_{20}$ from oxalates

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A barium titanate precursor with barium: titanium ratio of 2: 9 was prepared by coprecipitation of mixed barium and titanium chlorides with ammonium oxalate aqueous solution at pH 7-7.5. Single-phase of $Ba_2Ti_9O_{20}$ crystallised in the triclinic system and dense ceramic are obtained by sintering at 1375 °C for 4-8.5 h. The grain size of the sintered ceramics is 3 to 5 µm. Dielectric properties of the sintered ceramics in the microwave frequency region were measured using the $TE0_{11}$ mode. Good microwave characteristics for $Ba_2Ti_9O_{20}$ were found. At 5 GHz, the dielectric constant and the dielectric loss (tgδ) were 36 respectively, $0.6x10^{-3}$. The quality factor due to dielectric loss at 5 GHz was ~ 1 700.

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1. Introduction

Dielectric ceramics for microwave resonator applications have been intensively studied. Dielectric resonators are main components in microwave subsystems which are used in commercial products including satellite receiver modules and cellular telephones. The main aim of the researches in this field is to develop improved microwave components (with increased dielectric constant and reduced dielectric loss). In order to achieve these aims there are two ways: improving the properties of the existing materials by carefully controlling the processing techniques and, doping the existing materials.

Titania-rich compounds in the BaO-TiO_2 system (such as $BaTi_4O_9$ and $Ba_2Ti_9O_{20}$) are used for manufacture of miniaturized microwave resonators with high dielectric constants [1-5]. The synthesis of $Ba_2Ti_9O_{20}$ monophasic ceramics is difficult because there are various thermodynamically stable compounds in the vicinity of the desired composition (2BaO-9TiO_2) [6]. In the preparation of $Ba_2Ti_9O_{20}$ material by mixed oxide method from $BaCO_3$, BaO or $BaTiO_3$ and TiO_2, the $BaTi_4O_9$ intermediate phase always is formed preferentially [4, 7, and 8]. O'Bryan and Thomson [9] stated that the $Ba_2Ti_9O_{20}$ phase is stable in the temperatures ranging from 1300 to 1420 °C. Wen-Yi Lin et al. [10], prepared stabilized $Ba_2Ti_9O_{20}$ with SnO_2, by sintered at 1360-1390 °C for 5 h. Because of the difficulties of the synthesis of $Ba_2Ti_9O_{20}$ by a solid state reaction route, some alternative methods such as coprecipitation [11, 12] and sol-gel [13-16] were used.

In the present work, the coprecipitation method of mixed barium and titanium chlorides solutions with ammonium oxalate was used to prepare single-phase $Ba_2Ti_9O_{20}$ ceramics. The microstructure and microwave dielectric properties of these ceramics were investigated.

2. Experimental procedure

Dibarium nonatitanate oxide named also, barium 20-oxo-nonatitanate ($Ba_2Ti_9O_{20}$) was prepared by coprecipitation method starting from $BaCl_2 \cdot 2H_2O$, $TiCl_4$ and $(NH_4)_2C_2O_4 \cdot H_2O$ as shown in Fig.1.

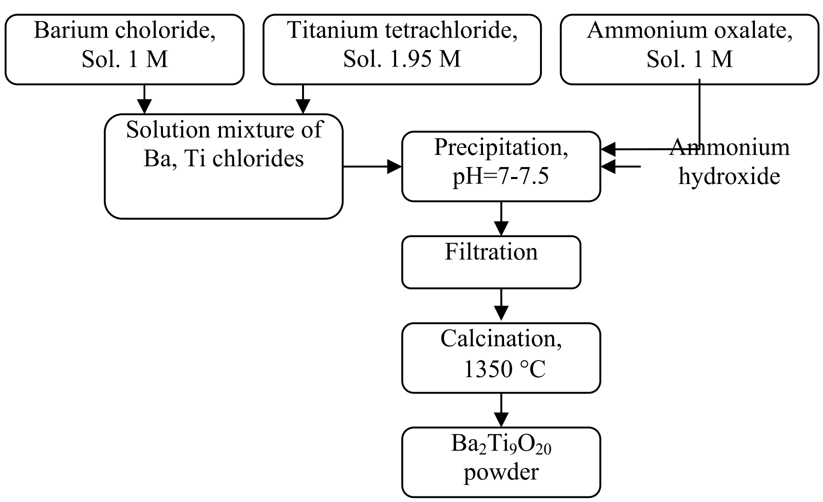

Fig. 1. Flow sheet of $Ba_2Ti_9O_{20}$ synthesis by coprecipitation method.

An aqueous solution of titanium tetrachloride (1.95 M) was prepared, as described by Kudaka and Chang [17-20], by adding distillate water to titanium tetrachloride at 4 °C. The solution of barium chloride (1 M) and ammonium oxalate were prepared at 80 °C. The mixed solution of barium chloride and titanium tetrachloride was added to the aqueous solution of ammonium oxalate (molar ratio Ba^{2+}:Ti^{4+}:$C_2O_4^{2-}$ = 2:9:11.2) to obtain the precipitate. The experimental conditions for this reaction were chosen as follows: (i) the reaction temperature was 80 °C, (ii) the pH solution was maintained in the range of 7-7.5 by adding ammonium hydroxide, and (iii) the rate of titration was 10 mL/min. After filtration, the precipitate was washed with slightly ammoniated water (pH=8) to avoid the loss of Ba^{2+} and Ti^{4+}. Washing was done to completely eliminate the Cl^- and $C_2O_4^{2-}$ ions. Then, the precipitate was dried at 100 °C and calcined at various temperatures (up to 1350 °C). The calcined $Ba_2Ti_9O_{20}$ powder was pressed into disks at a pressure of 200 MPa and sintered at 1375 °C for 4 h and, 8.5 h in air. Samples have been characterized using XRD, Raman spectroscopy, SEM and dielectric properties at microwave frequency measurements. The structure of the sintered ceramics was characterized by X-ray diffraction technique using a Shimadzu X-Ray Diffractometer XRD-6000. CuKα1 radiation, (wavelength 1.5406), a LiF crystal monochromator and Bragg-Brentano diffraction geometry were used. The data were acquired at 25 °C with a step-scan interval of 0.020 ° and a step time of 10 s. The Raman spectrum was recorded at room-temperature using a spectrometer R–2001™. The 785 nm line of a laser operating at 500 mw was used for excitation. The unpolarized radiation was collected with an instrumental resolution of 30 cm^{-1}. The microstructure of the samples was investigated using a Hitachi S-2600N Scanning Electron Microscope. Before the microwave measurements, the surfaces of the disk-shaped samples were polished with sandpaper. The dielectric properties at microwave frequency were measured by the resonant cavity method described by Hakki and Coleman [21] using the TE011 propagation mode coupling with an adjustable parallel plate cavity and a scalar network analyzer (Model 9855 B, Hewlett-Packard, Palo Alto, CA).

3. Results and discussion

3.1. XRD analysis

Fig. 2 shows the X-ray diffraction patterns (CuK_α radiation) for B_2T_9 ceramic sintered at 1375 °C for 4 h in air.

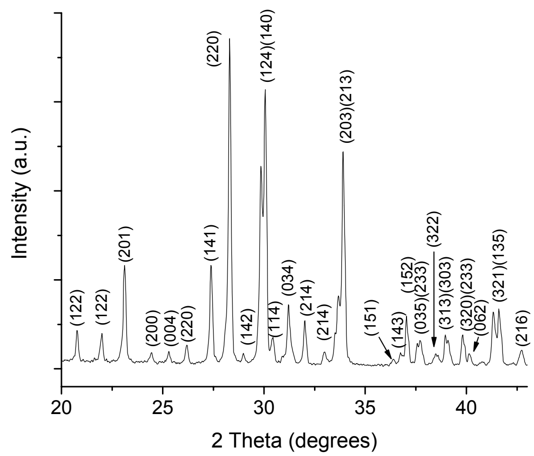

Fig. 2. XRD of $Ba_2Ti_9O_{20}$ ceramic sintered at 1375 °C in air.

All the XRD peaks are indexed for the single phase of $Ba_2Ti_9O_{20}$, crystallised in the triclinic system [22]. The x-ray diffraction patterns in figure 2 illustrate that the conversion of the oxalate coprecipitate into the Hollandite-like $Ba_2Ti_9O_{20}$ is completed at 1375°C/4h.

3.2. Raman spectroscopy

Fig. 3 shows the Raman spectrum of $Ba_2Ti_9O_{20}$ ceramic sintered at 1375 °C in air, recorded at room temperature, in the range of 150 to 1000 cm^{-1}.

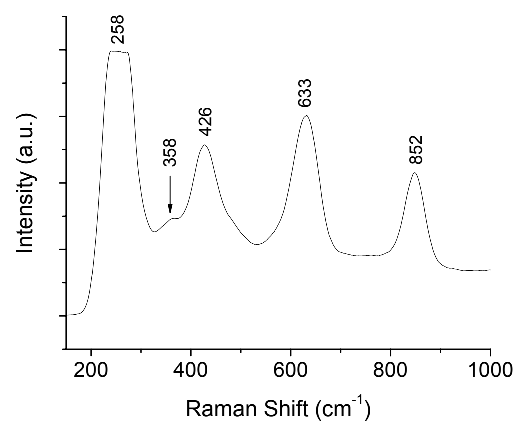

Fig. 3. Raman spectrum of $Ba_2Ti_9O_{20}$ ceramic sintered at 1375 °C in air.

This spectrum presents peaks at 258, 358, 426, 633 and 852 cm^{-1}. In good agreement with the literature data [2, 23], these peaks indicate the $Ba_2Ti_9O_{20}$ phase. No other peaks were detected in the Raman spectrum, suggesting that the sample consists of single phase $Ba_2Ti_9O_{20}$, in conformity with XRD data (Fig.2).

3.3. SEM analyse

It's known that the granular structure of the $Ba_2Ti_9O_{20}$ ceramics has a significant effect on their microwave dielectric properties [24]. For this reason, we observed by SEM microscopy the ceramic pellets and not the powders of $Ba_2Ti_9O_{20}$. The structure of the sintered samples (1375 °C/8.5h) is shown in Fig. 4.

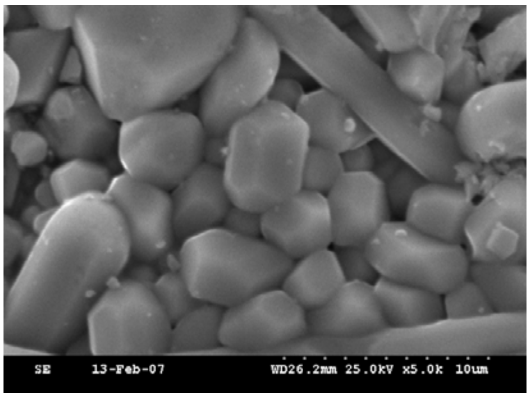

Fig. 4. SEM photomicrograph of $Ba_2Ti_9O_{20}$ ceramic sintered at 1375 °C in air.

As can be seen, the grains are of equi-axed geometry, well shaped and the grain size is quite uniform (3-5 μm). However, some large grains are present. The pores seen in figure 4 suggest an incomplete densification of the sample.

The density of the sintered ceramic was determined using Archimed's principle (in water). The theoretical density (TD) of the B_2T_9 crystal (ρB_2TS_9=8.47 g/cm^3) was calculated from the chemical formula and unit cell data, using the relationship: density = (1.66 x formula weight x Z) / unit cell volume, where Z is the number of molecules in the unit cell. B_2T_9 ceramic samples show densities of about 7.24 g/cm^3, (86% TD) and 7.75 g/cm^3, (92% TD) when the sintering time was 4 h, respectively 8.5 h. The samples were sintered at 1375 °C in air.

3.4. Microwave dielectric properties

The relative densities and dielectric properties of sintered $Ba_2Ti_9O_{20}$ samples are presented in Table I as function of the sintering conditions.

Table 1. The relative densities and dielectric properties of $Ba_2Ti_9O_{20}$ ceramics.

Material / Relative density, (%TD)	f_r, (GHz)	Δf, (GHz) x10^{-3}	ε_r	tgδ, x10^3	Q
$Ba_2Ti_9O_{20}$-(1) / 86	6.9743	17.02	33.8	2.0	500
$Ba_2Ti_9O_{20}$-(2) / 92	4.9018	2.9747	35.9	0.6	1667

The sintered density increased with the heat sintering time at 1375 °C and in the same way increased the microwave dielectric constant (K) of the sintered $Ba_2Ti_9O_{20}$ samples. Since the typical dielectric constant of a fully densified pure Hollandite-like sintered $Ba_2Ti_9O_{20}$ material is around K~39.9 [24], the samples sintered at 1375 °C for 4 h have significantly lower K-value (K~33.8) than of the intrinsic $Ba_2Ti_9O_{20}$ material, indicating that the materials have not been fully densified. In contrast, a prolonged sintering time up to 8.5 h leads to K-value (K~35.9) which is close to that of the typical $Ba_2Ti_9O_{20}$ material, indicating that the Hollandite-like phase has been well developed as shown the SEM micrograph (Fig.4). Even in this case, the presence of the pores suggests that the samples are not yet fully densified, possibly also due to the pressing conditions.

4. Conclusions

The coprecipitate of barium and titanium ions (Ba^{2+}:Ti^{4+} = 2:9) in an aqueous solution at pH7-7.5 was prepared. Bulk XRD analysis and Raman spectroscopy indicated that the ceramics sintered at 1375 °C consist of triclinic $Ba_2Ti_9O_{20}$ single phase (Hollandite). The grains of the sintered ceramics are of equi-axed geometry, well shaped and the size is quite uniform (3-5 μm). Some large grains and pores are present. The dielectric properties in the microwave region of the $Ba_2Ti_9O_{20}$ ceramic are in good agreement with the literature [23].

References

[1] T. Negas, G. Yeager, S. Bell, N. Coats, Am. Cewram. Soc. Bull. **72**(1), 80 (1993).
[2] J. Javadpour, N. G. Eror, J. Am. Ceram. Soc. **71**(4), 206 (1988).
[3] D. J. Masse, R. A. Purcel, D. W. Ready, E. A. Maguire, C. P. Hartwig, Proc. IEEE **59**(11), 1628 (1971).
[4] H. M. O'Bryan Jr., J. K. Plourde, J. Thomson Jr., D. F. Linn, J. Am. Ceram. Soc. **57**(10), 450 (1974).
[5] D. W. Readey, E. A. Maguire, C. P. Hartwig, D. J. Masse, Tech. Rept. ECOM-0455-F, Raytheon Co., Waltham, MA, June 1971
[6] H. M. O'Bryan, J. Thomson, J. Am. Ceram. Soc. **66**(1), 66 (1983).
[7] J. J. Ritter, R. S. Roth, J. E. Blendell, J. Am. Ceram. Soc. **69**, 155 (1986).

[8] K. W. Kirby, B. A. Wechsler, J. Am. Ceram. Soc. **74**(1), 1841 (1991).
[9] H. M. O'Bryan, J. Thomson, J. Am. Ceram. Soc. **57**, 522 (1974).
[10] W. Y. Lin, R. A. Gerhardt, R. F. Speyer, J. Y. Hsu, J .Mater. Sci. **34**(12), 3021 (1999).
[11] J. M. Wu, H. W. Wang, J. Am. Ceram. Soc. **71**, 869 (1988).
[12] C. L. Whu, G. H. Hsiue, Y. J. Chiang, K. S. Liu, I. N Lin, J. Eur. Ceram. Soc. **24,** 1781 (2004).
[13] H. Lu, L. Burkhart, G. Schrader, J. Am. Ceram. Soc. **74,** 968 (1991).
[14] J. H. Choy, Y. S. Han, J. H. Sohn, M. Itoh, J. Am. Ceram. Soc. **78**, 1169 (1995).
[15] Y. B. Xu, X. M..Chen, L. B. Wang, J. Am. Ceram. Soc. **84**, 669 (2001).
[16] W. Li, N. Wang, W. J. Wu, Y. L. Wang, M. Y. Zhao, Mater. Lett. **59**, 162 (2005).
[17] T. T. Fang, H. B. Lin, J. Am. Ceram. Soc. **72**(10), 1899 (1989).
[18] T. T. Fang, H. B. Lin, and J. B. Hwang, J. Am. Ceram. Soc. **73**(11), 3363 (1990).
[19] F. S. Yen, C. T. Chang, Y. H. Chang, J. Am. Ceram. Soc. **73**(11), 3422 (1990).
[20] K. Kudaka, H. Iizumi, K. Sasaki, J. Am. Ceram. Soc. Bull. **61**(11), 1236 (1982).
[21] B. W. Hakki, P. D. Coleman, IRE Trans. Microwave Theor. Tech. **8**, 402 (1960).
[22] E. Tillmanns, W. Hofmeister, W. H. Baur, J. Am. Ceram. Soc. **66**, 268 (1983); Pattern 76-1538.
[23] H. C. Lu, L. E. Burkhart, G. L. Schrader, J. Am. Ceram. Soc. **74**, 968 (1991).
[24] C. Li, G. H. Hsiue, I. N. Lin, Y. C. Chen, Nanotechnology, **17**(1), 185 (2006).

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